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Carbonium Ion Polymerization of Norbornene and Its Derivatives

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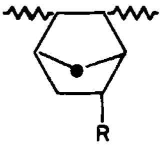
Summary

Cationic polymerizations of various bicyclo-(2,2,1)-heptane olefinic derivatives were examined, and the structures of the resulting polymers determined. Norbornene readily polymerizes to soluble polymer at −78°C, whereas 2-vinyl-5-norbornene yields predominantly soluble polymer at low temperatures (~ −78°C) and largely cross-linked product at higher temperatures (~ −30°C). The major polymerization mechanisms for norbornene and 2-vinyl-5-norbornene are similar. In each case, the reaction proceeds by opening of the endo double bond, and the repeat units are



where R is H or vinyl. The reactivity difference between the endo and exo double bonds in 2-vinyl-5-norbornene is most likely due to the strained endo double bond. When the reactivity of the exo bond is enhanced by the introduction of a methyl group (2-isopropenyl-5-norbornene) both double bonds participate simultaneously in the polymerization, and cross-linked products are obtained.

Competition experiments showed that 2-methylenenorbornane is more reactive toward carbonium ions than norbornene.

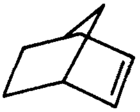
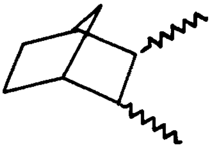
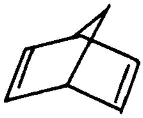
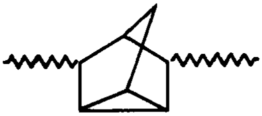
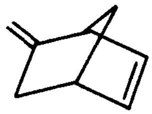
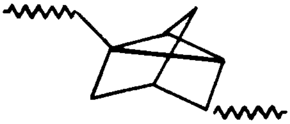
Spectroscopic (IR) studies confirm the structure of poly(2-methylene-5-norbornene) proposed earlier by others.

The polymerizabilities of bicyclo-(2,2,1)-heptane olefinic derivatives and cycloolefins under cationic conditions are compared.

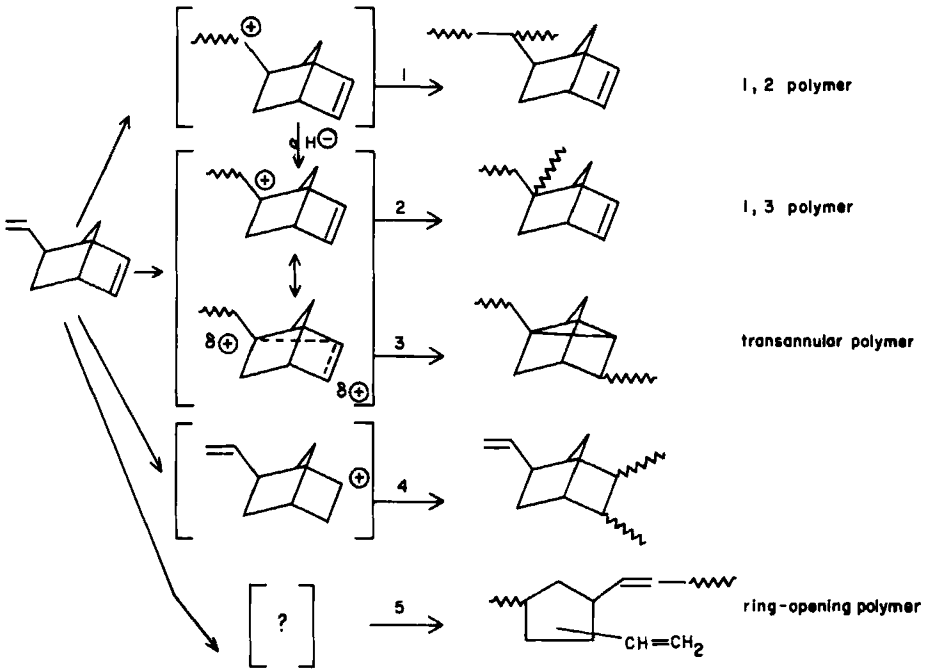
The polymerizations of various bicyclo-(2,2,1)-heptene (norbornene) derivatives via an ionic mechanism have been investigated recently by several workers. Thus the ionic polymerizations of norbornene (*1–5*), 2-methylene-5-norbornene (*5,7*), and norbornadiene (*6*) have been studied, and the structures of the resulting, sometimes unexpected, repeat units have been established. Table 1 summarizes some of the more important developments in this field.

TABLE 1

Ionic Polymerization of Norbornene Derivatives

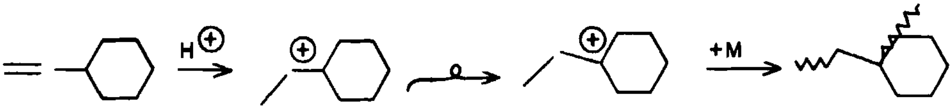
Monomer	Polymer repeat unit	Refs.
 **Norbornene**		*1*, 2
		*1–4*
 **Norbornadiene**		*6*
 **Methylenenorbornene**		*5, 7*

In the course of our fundamental studies on carbonium ion polymerization, it was of interest to examine the mechanism of 2-vinyl-5-norbornene polymerization. This monomer offers at least five relatively simple possibilities for homopolymerization:

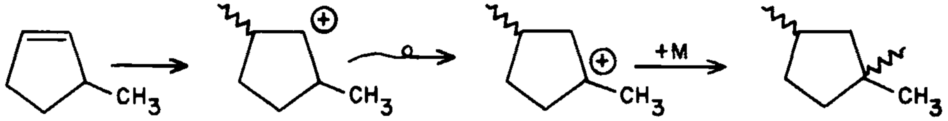


Route 1 is a simple cationic vinyl polymerization and is self-explanatory.

Route 2 involves intramolecular hydride shift; i.e., the secondary carbonium ion isomerizes via hydride migration to a more stable tertiary cation, the true propagating species. Similar hydride shift polymerizations occur with vinylcyclohexane (8),



and 3-methylcyclohexene or cyclopentene (9),



Route 4 involves a simple addition to the strained endo double bond and is self-explanatory.

Finally, route 5 shows the possibility of a ring-opening polymerization as discussed in detail by other workers (*1–4*).

This paper is concerned with the cationic polymerization mechanism of norbornene, 2-vinyl-5-norbornene, and other norbornene derivatives, and with the relative polymerizabilities of several norbornene and norbornane derivatives.

EXPERIMENTAL

Monomers

Norbornene was obtained from the Aldrich Chemical Co. and was used as received.

2-Vinyl-5-norbornene, 2-isopropenyl-5-norbornene, and 2-methylenenorbornane were synthesized *via* the Wittig reaction from methylene triphenyl phosphorane and 2-formyl-5-norbornene, 2-acetyl-5-norbornene, and norcamphor, respectively. In each case, the modification of the Wittig reaction according to Corey and coworkers (*10,11*) was utilized. Methyl sulfinyl carbanion was first prepared from sodium hydride and dimethyl sulfoxide, and the resultant solution was treated with methyl triphenyl phosphonium bromide to form methylene triphenyl phosphorane. The carbonyl compound in dimethyl sulfoxide solution was then added, and the reaction product was worked up as described (*11*).

For the preparation of these bicyclo diolefins the starting carbonyl compounds were obtained as follows:

Norcamphor was obtained from the Aldrich Chemical Co. and was used as received.

2-Formyl-5-norbornene was prepared in 94% yield according to the procedure of Diels and Alder (*12*). $n_D^{25} = 1.4868$. G.C. analysis: exo isomer, 22.8%; endo isomer, 73.6%; unidentified impurities, 1.2%.

2-Acetyl-5-norbornene was prepared in 92% yield via the Diels-Alder reaction of cyclopentadiene with methyl vinyl ketone. $n_D^{20} = 1.4852$ [lit. 1.4880 (*13*)]. G.C. analysis: exo isomer, 18.1%; endo isomer, 79.8 %; unidentified impurities, 2.1%.

2-Vinyl-5-norbornene was prepared in 46% yield. B.p., 73 to 73.1°C/76 mm $n_D^{20} = 1.4811$ G.C. analysis: one peak, 99.9%.

2-Isopropenyl-5-norbornene was prepared in 71% yield. B.p., 73°C/25 mm $n_D^{20} = 1.4867$. G.C. analysis: exo isomer, 36.5%; endo isomer, 60.2%; unidentified impurities, 3.2%.

2-Methylenenorbornane was prepared in 49% yield. B.p., 60 to 60.1°C/76 mm $n_D^{20} = 1.4742$. G.C. analysis: 96.6% product; 3.4% light hydrocarbons.

G.C. Analyses

A Perkin-Elmer Model 226 G.C. with flame-ionization detector was used for all analyses. 2-Formyl-5-norbornene (temperature-programmed) and 2-acetyl-5-norbornene (isothermal) were analyzed with a 300-ft 0.01-in. I.D. open tubular column coated with Carbowax 1540.

Injection block temperatures were kept at 175°C and below. At higher temperatures cracking patterns were obtained.

Temperature programming from lower temperatures was used for the bicycloolefins, which required more resolution to separate the endo-exo isomers. These compounds were analyzed with a 300-ft 0.01-in. I.D. open tubular column coated with DC-550 silicone oil. 2-Vinyl-5-norbornene was analyzed under isothermal and temperature-programmed conditions. In no case could a splitting of the major peak (99.9%) be obtained. If endo-exo isomers were present in this material, they were not resolved under the analytical conditions.

Polymerizations

Polymerizations were carried out in a stainless-steel enclosure under nitrogen atmosphere. All monomers were freshly distilled before polymerization. Ethyl chloride solvent and aluminum ethyl dichloride catalyst were used. The monomer and solvent were mixed, thermoequilibrated at the selected temperature level, and the catalyst solution was added gradually with agitation. Reactions were terminated by the introduction of prechilled methanol. The products were separated by centrifuging, washed three times with methanol, and dried *in vacuo* for 72 hr at 50°C. Product solubilities were determined by extraction with toluene at room temperature.

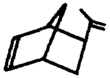
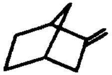
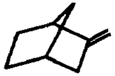
Norbornene and 2-vinyl-5-norbornene polymerizations were carried out in the temperature range −30 to −135°C.

The polynorbornenes were completely toulene soluble. Poly(2-vinyl-5-norbornene) prepared at −78° was largely soluble in this solvent, whereas that prepared at −30° was sparingly soluble (Table 2).

TABLE 2

Polymerization of Norbornene Derivatives

Monomer			Solvent C_2H_5Cl, ml	$AlEtCl_2$ catalyst added			Temp., °C	Time, min	Yield		Softening range	$\bar{M}_n$[a]	Solubility	Physical appearance
Formula	ml	g		ml	g	Moles × 10^2			g	% conv.				
	—	3.26	4	2.68[b]	0.165	0.13	−100	233	0.133	4.1	260–275	1945	Toluene soluble	White powder
	—	4.026	5	2.6[b]	0.165	0.13	−78	1080	2.147	53	235–247	1475	Toluene soluble	White powder
	5.0	5.65	7.0	0.4[c]	0.0098	0.008	−135	19	No polymer					
	0.08	0.09	0.12	0.7[c]	0.017	0.0135	−135	18	No polymer					
	0.08	0.09	0.12	0.5[c]	0.0123	0.01	−100	10	No polymer					
	4.52	5.11	6.7	4.4[c]	0.108	0.085	−78	1500	0.506	9.9	330	4023	78% soluble in toluene	White powder
	0.5	0.57	0.5	0.3[b]	0.018	0.0145	−30	34	0.180	32				White powder
	3.2	3.62	3.2	1.0[b]	0.062	0.048	−30	77	0.907	25	275		8.5% soluble in toluene	White powder

	0.2	0.22	—	0.025^b	0.0015	0.0012	−30	2	0.0314	14.2	Insoluble in toluene	Yellow brittle film
	3.0	3.36	3.0	0.43^b	0.026	0.0002	−30	23	0.296	8.8	Insoluble	Yellow brittle film
	0.5	0.56	1.0	0.15^b	0.009	0.007	−100	18	0.070	12.5	Insoluble	Yellow, hard, tough
	3.0	3.36	6.0	0.93^b	0.057	0.045	−100	114	0.203	6.0		Yellow, hard, tough
	0.5	0.56	1.0	0.28^b	0.017	0.013	−78	25	0.136	24		Brown, hard, tough
	0.2	0.23	—	0.15^b	0.009	0.0073	−30	7	0.115	50		Yellow viscous oil
	3.0	3.48	3.0	0.48^b	0.029	0.0023	−30	66	2.136	61		Yellow viscous oil
	3.0	3.48	3.0	2.4^b	0.15	0.0012	−100	300	No polymer			
	3.0	3.48	3.0	1.5^b	0.002	0.073	−78	1500	2.116	61		Hazy oil

[a] $\bar{M}_n$ by osmometry.

[b] Catalyst solution concentration: 0.385 mole $AlEtCl_2$/liter C_2H_5Cl.

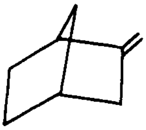
[c] Catalyst solution concentration: 0.158 mole $AlEtCl_2$/liter C_2H_5Cl.

2-Isopropenyl-5-norbornene and 2-methylenenorbornane were polymerized with $AlEtCl_2$ at −100, −78, and −30°C. Insoluble products were obtained with the former, and viscous oils with the latter monomer. 2-Methylene-5-norbornene was polymerized with $AlCl_3$ in ethyl chloride catalyst at −130°C.

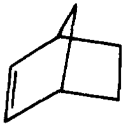
The toluene-soluble polymer fractions were analyzed by IR and NMR spectroscopy. These analyses were performed with a Beckman (in usual KBr pellet technique) and with a Varian 60 instrument, respectively. X-ray patterns were obtained with a Norelco diffractometer (goniometer scanning).

Competition Experiments

The following system was prepared:



1.35 g



1.17 g

n-heptane 10 ml

This system, containing equimolar amounts of monomers, was polymerized with 2.60 ml $AlEtCl_2$ in ethyl chloride catalyst solutions (concn.: 0.385 mole $AlEtCl_2$/liter) for about 200 min at −78°C and then terminated with 35 ml methanol. Concurrently an appropriate control system was prepared without catalyst addition. Reactions were terminated with methanol, and the systems were analyzed by gas chromatography. A Perkin-Elmer 226 instrument with a 300-ft 0.01-I.D. column (40# He) coated with Carbowax 1540 at 100°C was used.

Results

The results are summarized in Table 2.

The infrared spectra of polynorbornene and poly(2-vinyl-5-norbornene) obtained at −78°C are shown in Figs. 1 and 2. Band assignments for poly(2-vinyl-5-norbornene) are compiled in Table 3.

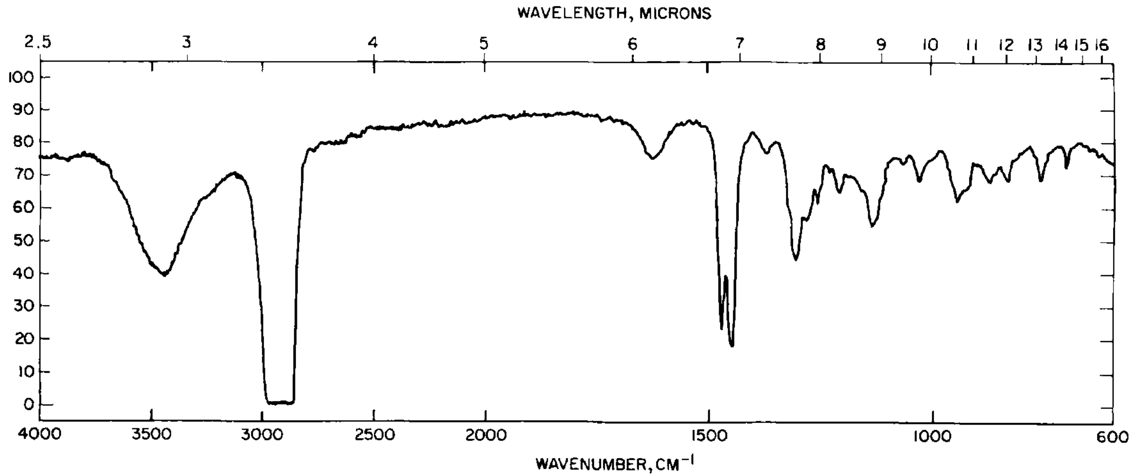


FIG. 1. Infrared spectrum of polynorbornene.

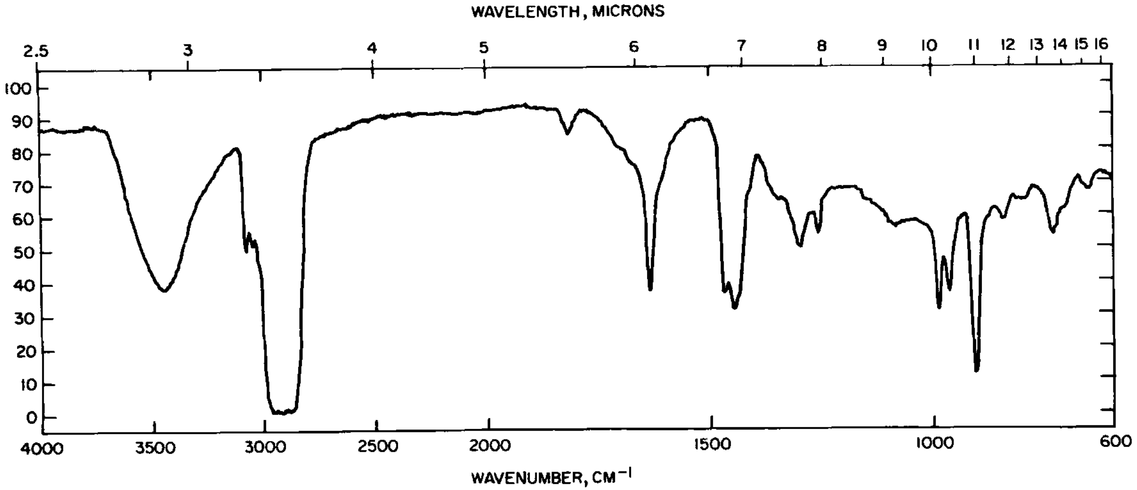


FIG. 2. Infrared spectrum of poly(2-vinyl-5-norbornene).

TABLE 3

Infrared-Band Assignments of Poly(2-vinyl-5-norbornene)
(Polymer prepared at −78°C)

Wave number cm^{-1}	Intensity[a]	Assignment
3070	W	CH (olefinic)[b]
3045	W	CH (olefinic)[b]
2940	S	CH (aliphatic)
2860	S	CH (aliphatic)
1815	W	Vinyl olefin[b]
1700	W (diffuse)	Vinyl olefin[b]
1680	VW	Internal olefin
1630	S	Vinyl (major band)[b]
1610	Shoulder	Vinyl (major band)[b]
1460	S	Various methylenes $-CH_2-$[b]
1440	S	Various methylenes $-CH_2-$[b]
1430	S	Various methylenes $-CH_2-$[b]
1350	W (diffuse)	Tert. $-\overset{\vert}{\underset{\vert}{C}}-H$
1290	M	Ring with a substituent
1250	M	Polar-ring substituent
1155	VW	Adjacent tert. $-\overset{\vert}{\underset{\vert}{C}}-H$
1125	VW	Adjacent tert. $-\overset{\vert}{\underset{\vert}{C}}-H$
1080	M (diffuse)	Adjacent tert. $-\overset{\vert}{\underset{\vert}{C}}-H$
980	M	Vinyl olefin
960	M	Tert. $-\overset{\vert}{\underset{\vert}{C}}-H$ in a condensed ring system (and/or internal *trans* type II olefin)
900	S	Vinyl olefin
835	W	Multiple substituents on ring
790	W	Bicyclic structure in a linear chain
735	M	Short saturated chain[c] and/or *cis* type II internal olefin in the chain
725	M	Long saturated chain[c]
710	M	Long saturated chain[c]
650	M	Vinyl olefin

[a] W, weak; M, medium; S, strong; VW, very weak.

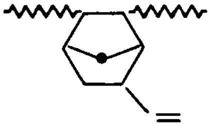
[b] Similar to vinyl cyclopentane, i.e., vinyl side chain on a ring.

[c] Similar to low-temperature polynortricyclene (*6*).

The infrared spectrum of polynorbornene suggests that the predominant repeat structure is

This polymer is most likely very similar to that obtained earlier by Italian workers, who employed a complex catalyst mixture of the Ziegler-Natta type (*1*).

Analysis of the IR spectra suggests the following repeat unit for poly(2-vinyl-5-norbornene):

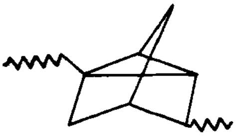


The most important structural assignment in the spectrum is the strong vinyl unsaturation indicated by bands at 900, 980, 1630, and 1815 cm^{-1}. The intensities and band structures are very similar to those observed with vinyl cyclopentane. The simplicity of the spectrum indicates a symmetrical structure.

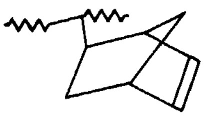
Examination of the spectra of a number of condensed ring structures, e.g., bicyclo(2,2,1)heptane and *cis*-bicyclo(3,3,0)octane indicates absorptions in the 960-cm^{-1} region. Consequently, the band at 960 cm^{-1} is assigned to a condensed ring system rather than to an internal double bond (*trans*) structure.

The spectrum of 2-vinyl-5-norbornene monomer shows a very strong absorption at 710 to 720 cm^{-1}, indicating the presence of a *cis* internal double bond (exo and/or endo substitution). In contrast, the spectrum of the polymer shows a very weak absorption in this region; in fact, only a shoulder at 710 cm^{-1} appears on the 725-cm^{-1} band. The same type of double band has already been observed in the spectrum of polynortricyclene obtained in low-temperature polymerization (6) and is interpreted as a long saturated chain structure rather than unsaturation.

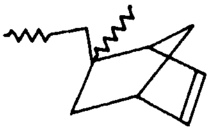
The fact that no strong absorption is observed in the 850-cm^{-1} region indicates the absence of



The absence of unsaturation other than vinyl eliminates the following repeat structures:



and



The structure of the triplet at ~ 1450 cm^{-1} is very similar to that in vinylcyclopentane for the saturated portion of this molecule. The diffuse, medium-intensity bands at ~ 1350 and 1080 cm^{-1} indicate appreciable amounts of tertiary hydrogens, including adjacent tertiary hydrogens. The bands at 1290 and 735 cm^{-1} indicate the presence of one or two or more substituents on a ring, respectively.

The spectrum of a poly(2-vinyl-5-norbornene) synthesized at $-30°C$ was analyzed and compared to a sample prepared at $-78°C$. Table 4 shows the changes in intensities of infrared absorptions.

One of the major differences observed between the spectra of poly(2-vinyl-5-norbornene) prepared at -78 and $-30°C$ is the consistent decrease of the bands associated with the vinyl group in the $-30°C$ sample. Conversely, bands assocated with internal olefins in a chain became quite pronounced in the sample prepared at the higher temperature.

Another significant observation is that the nature of adjacent $-\overset{|}{\underset{|}{C}}-$H's changed, as indicated by the multiplicity of the bands associated with tertiary hydrogens. For example, in the polymer made at $-78°C$ the major $-\overset{|}{\underset{|}{C}}H$ band appears at 1080 cm^{-1}, whereas in that prepared at $-30°C$ this band decreased somewhat in intensity with more pronounced bands appearing at 1155 and 1122 cm^{-1}. The broad band at 790 (± 10) cm^{-1} appearing in the sample prepared at $-78°C$ was absent in the sample obtained at $-30°C$.

Since the structure of the low-temperature sample is probably more regular than that of the high-temperature one, the 800-cm^{-1} band is tentatively assigned to a composite absorption, possibly indicating a linear sequence of saturated bicyclic units in the chain. A similar very strong band was found earlier in polynortricyclene and was interpreted in a similar manner (6).

In summary, these observations indicate the following changes

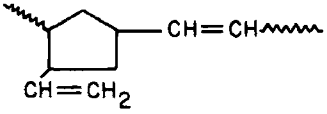
TABLE 4

Changes in Infrared Absorptions Due to Increasing the Polymerization Temperature from −78 to −30°C

Wave number, cm^{-1}	Change in intensity	Assignment
3045	Increased	$-CH{=}C\begin{smallmatrix}/\\ \backslash\end{smallmatrix}$ (olefinic CH)
1710	New band	CO (oxidation during extraction)
1680	Increased	Internal olefin
1630	Decreased	Vinyl olefin
1370	New band	Tert. $-\overset{|}{\underset{|}{C}}-H$
1250	Decreased	Polar substituent (assoc. with vinyl group)
1155	Increased	Tert. $-\overset{|}{\underset{|}{C}}-H$
1125	Increased	Tert. $-\overset{|}{\underset{|}{C}}-H$
1080	Decreased	Tert. $-\overset{|}{\underset{|}{C}}-H$
960	Increased	Probably *trans* type II olefin
900	Decreased	Vinyl
790	Absent	Bicyclic structure in a linear chain
735	Increased	*Cis* type II in an open chain

in polymer structure due to increased polymerization temperature: (a) less vinyl groups, (b) more internal olefins in the chain, (c) multiplicity of $-\overset{|}{\underset{|}{C}}-H$ structure, and (d) less regular structure.

Apparently the major polymerization mechanism at −30°C still proceeds by the opening of the internal double bond as proposed above for the sample obtained at −78°C. At higher temperatures the vinyl groups also participate, which leads to bands associated with a less regular structure (i.e., branching or copolymerization of different units) and with the multiplicity of tertiary hydrogens. The marked increase in absorption at 735 cm^{-1} together with the moderate increase in absorption at 960 cm^{-1} (indicating in-chain unsaturation) may be due to contributions by



units.

If *cis* type II olefin were present in the polymer, such as appears in the bicyclic ring structure, the absorption due to this type of olefin would appear as in the pure monomer at 710 or 720 cm^{-1}, depending on whether the vinyl substituent is exo or endo. The fact that the olefin band appears at 735 cm^{-1} indicates that ring opening occurs. In addition, ring opening should produce some internal *trans* olefin in the polymer; and, indeed, increased absorption, attributable to this unsaturation, is observed at 960 cm^{-1}.

The NMR spectra of polynorbornene and poly(2-vinyl-5-norbornene) and the corresponding monomers have been analyzed. The spectrum of norbornene monomer shows a triplet at 5.86 ppm (J = 1.8 cps) for the olefinic protons and a multiplet at 2.75 ppm for the two bridgehead protons. The rest of the spectrum appears as a complex pattern between 0.7 and 1.85 ppm.

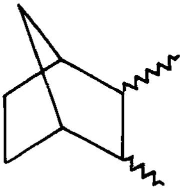
The NMR spectrum of polynorbornene in hexachlorobutadiene at ambient temperature does not show any olefinic protons. The bridgehead protons also have moved upfield to ~0.2 ppm. All the absorption from the polymer appears between 0.5 and 2.6 ppm. All these observations are consistent with the following repeat unit:

No significant difference was observed in the NMR spectra of polynorbornene samples synthesized at −78 or −100°C.

The NMR spectrum of poly(2-vinyl-5-norbornene) synthesized at −78°C was poorly resolved, yielding only a limited amount of information. Significantly, however, the spectrum showed the presence of 19.3% olefinic protons. (The monomer contains 41.7% olefinic protons, 5 out of 12.) This finding alone suggests that repeat units formed by routes 3 and 5 cannot be major constituents of the polymer. The transannular polymer (route 3) contains no olefinic protons, whereas the ring-opened polymer (route 5) contains as many as the monomer, 41.7%. The presence of 19.3% olefinic protons in the spectrum indicates that the average repeat unit contains 2.32 olefinic protons. This coincides more closely to repeat units formed either by routes 1 or 2, each of which contains two olefinic protons, rather than to a repeat unit by route 4, which contains 3 protons. Significantly, however, the olefinic absorption in the spectrum appears between 4.5 to 6.0 ppm, indicating terminal (vinyl) unsaturation. In contrast the internal olefinic protons in the monomer appear at 6.05 ppm. Thus the NMR spectrum of poly(2-vinyl-5-norbornene) also suggests the preponderance of repeat units formed by route 4, i.e., by the opening of the endo double bond.

DISCUSSION

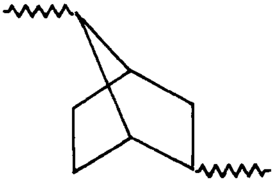
The structure of polynorbornene obtained in this work with $AlEtCl_2$ catalyst is probably very similar to that prepared with a cationic Ziegler catalyst (0.5 $AlBu_3/TiCl_4$) by Italian workers (*1*), who proposed the following repeat unit:



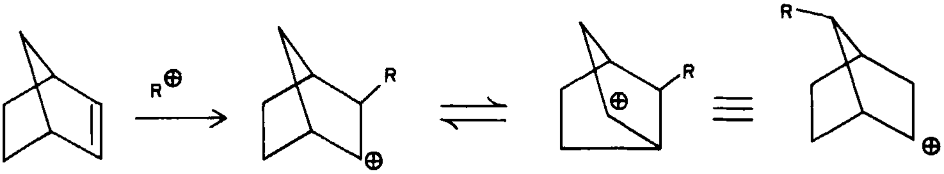
However, in contrast to this material, our product was not crystalline by X-ray analysis, in spite of the high softening ranges observed (cf. Table 2).

With anionic coordinated catalyst systems norbornene polymerizes via a ring-opening mechanism (*1*–*3*). The fundamentally different polynorbornene structures obtained with cationic or anionic catalysts may be useful as a diagnostic test to define the nature of unknown catalyst systems.

Theoretically at least, polynorbornene prepared with cationic catalysts could contain the structural unit

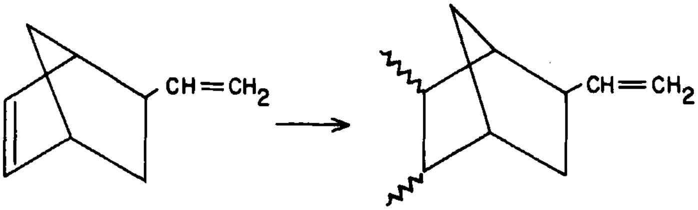


which could arise via rearrangement of the original carbonium ion:



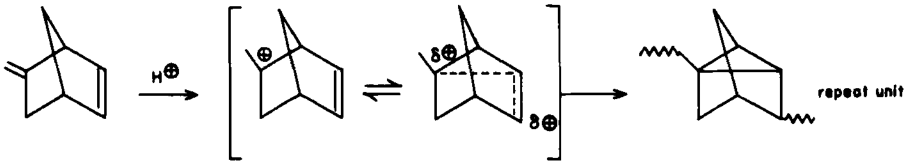
Available analytical evidence indicates that this structure is probably not a major unit in polynorbornene. Thus, 1,3-disubstituted cyclopentane shows a strong infrared absorption band at 985 cm^{-1}, but there is no band present at this wave number with polynorbornene. In addition, 1,2-disubstituted cyclopentane shows a pronounced band at 950 cm^{-1}, and there is an important absorption at this wave number in the spectrum of the polymer.

Spectroscopic evidence indicates that the low-temperature cationic polymerization of 2-vinyl-5-norbornene also proceeds predominantly by addition to the endo double bond:



Apparently the vinyl groups do not enter the polymerization at low temperature (−78°C), and the structure is remarkably "clean." At higher temperatures (~ −30°C) the vinyl group also enters the reaction, and cross-linked, insoluble polymers are formed. When the activity of the vinyl groups is enhanced by the introduction of an electron-releasing group, its reactivity approaches that of the strained endo double bond, so that both participate simultaneously in the reaction. Thus 2-isopropenyl-5-norbornene gives highly cross-linked products even at −100°.

2-Methylene-5-norbornene was polymerized at −130° to a white solid. The product started to soften at 82°, to melt at 213°, and to decompose at 255° before it was completely melted. According to infrared analysis, the over-all structure of the material was identical to that prepared by the Italian workers (7). For the mechanism we propose the following sequence:



The first proton (or carbonium ion) attack probably occurs at the methylene double bond, and a tertiary (homoallylic) carbonium ion is obtained. Simple propagation through the exo methylene group is inhibited because of the high steric compressions required (as discussed below for methylenenorbornene). However, in this case the less-hindered secondary homoallylic carbonium ion can provide the propagating site. Indeed, the structural analysis of the polymer corroborates this expectation.

2-Methylenenorbornane, in contrast to norbornene, gives only viscous oils (oligomers) in the −30 to −100° range. The structures of these viscous oils were not further investigated. However, these results prompted competitive experiments with 2-methylenenorbornane and norbornene.

Competitive experiments were carried out with equimolar mixtures of 2-methylenenorbornane and norbornene. Sufficient $AlEtCl_2$ catalyst was introduced to partially polymerize the more reactive monomer, and the remaining unreacted monomers were analyzed by gas chromatography. These experiments (cf. Table 5)

TABLE 5

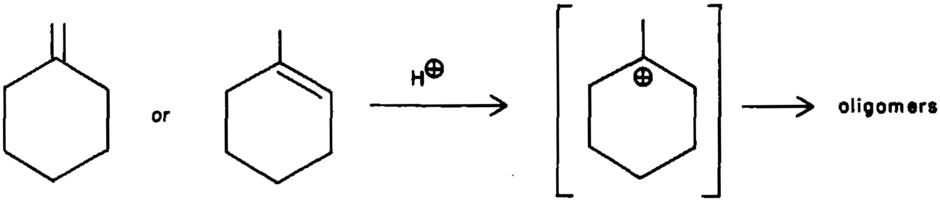
Relative Polymerizabilities of Norbornene and 2-Methylenenorbornane (Competitive Experiments)[a]

	Control (without catalyst)	Mixtures	
		1	2
n-Heptane	63.8	63.8	63.8
Norbornene	12.6	9.9	11.8
2-Methylenenorbornane	23.2	Trace	0.2

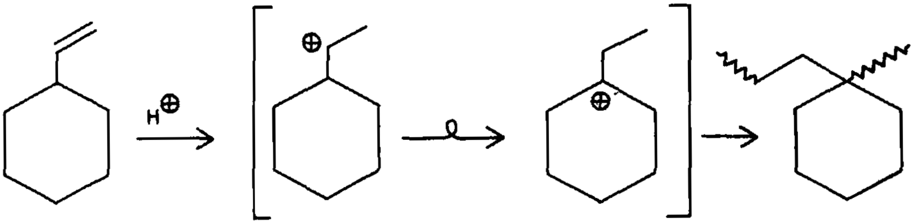
[a] For details see Experimental. Data in wt.-%.

showed conclusively that, under the experimental conditions, 2-methylenenorbornane was largely consumed, whereas substantial amounts of norbornene remained unconverted; i.e., 2-methylenenorbornane is more reactive than norbornene. This finding is not unexpected and is analogous to the greater reactivity of camphene to protonation than norbornene.

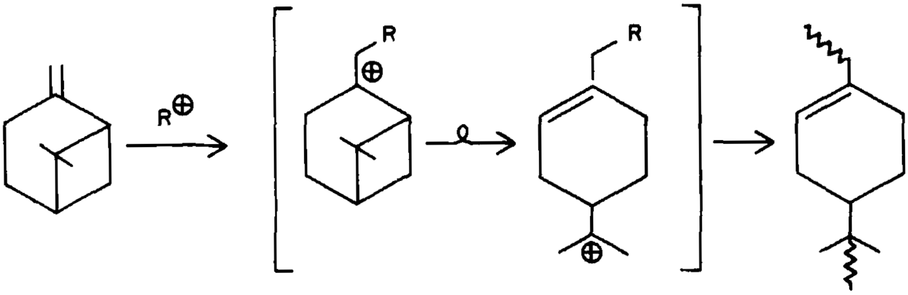
However, even though 2-methylenenorbornane is more reactive to protonation than norbornene, it is still less polymerizable. The oligomerization of 2-methylenenorbornane is identical to that of methylenecyclohexane and 1-methylcyclohexene, which also yield only oligomers (*14*):



On the other hand, with vinyl cyclohexane high polymer can be obtained—although not by direct addition but via intermediate hydride transfer (*2*):

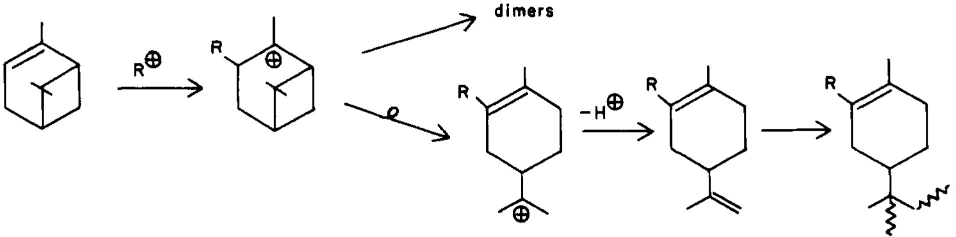


Similarly, β-pinene yields high polymer (*14*) but only by virtue of rearrangement:



This rearrangement is exoenergetic, because the strained four-membered ring is eliminated and a relatively stable internal double bond is obtained.

Polymerization of α-pinene also occurs via rearrangement but is different from β-pinene in that dimers and solid polylimonenes are obtained (5):



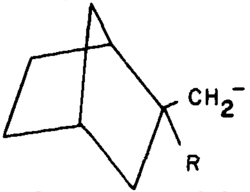
The initially formed ion rearranges and then deprotonates to a limonene derivative which is then polymerized via the external double bond. Alternatively, α-pinene is rapidly rearranged in one step to limonene followed by polymerization.

The relative polymerizabilities (as distinguished from reactivity to protonation) of norbornene and 2-methylenenorbornane can be related to a high-energy double bond in the former case and to unfavorable steric compression required during propagation in the latter case.

Internal double bonds are usually sluggish to polymerization—a phenomenon usually attributed to steric hindrance. Since norbornene can be polymerized to a fairly respectable molecular weight it might be deduced that the bridged structure restricts both the propagating carbonium ion and the incoming monomer unit to fixed, less-hindered positions, thereby allowing for propagation. However, reduction of steric factors per se is insufficient to explain the polymerizability of norbornene. Cyclopentene apparently cannot be polymerized cationically (9), and yet the steric factors inhibiting propagation should be less than with norbornene. In view of this, the polymerizability of norbornene must be largely attributable to its much higher energy double bond. The heat of hydrogenation of norbornene is 33.1 kcal/mole, compared with that of 25.7 kcal/mole for cyclopentene (*15*). The driving force provided by this highly strained double bond is demonstrated in the polymerization of 2-vinyl-5-norbornene, where, at low temperatures, polymerization proceeds exclusively via the endo double bonds.

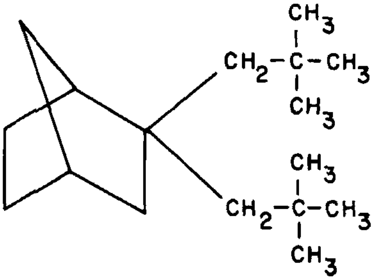
The oligomerization of 2-methylenenorbornane rather than polymerization to high molecular weight can be explained on the basis of unfavorable steric factors encountered during propagation. Protonated 2-methylenenorbornane should prefer to attack from its exo side, and the next monomer should prefer to be attacked from its exo side. An exo-endo combination is less preferred, and an endo-endo combination least preferred, because of the nonbonding interactions of the endo hydrogens in the norbornane structure. The ultimate steric factors inhibiting propagation are independent of mode of attack. On the other hand, the exo-exo combination is expected to be the most facile and will be considered here for the sake of simplicity.

When the protonated 2-methylenenorbornane adds to the incoming monomer a carbon-carbon bond is established in the exo position. At the same time a CH_3 group is forced into the relatively unfavorable endo position. At this stage steric factors are not severe; the methyl group is readily accommodated into the endo position. However, when the third monomer unit is to be incorporated, another carbon-carbon bond is established in the exo position of the second monomer unit, but now the very bulky methylenenorbornane moiety (from monomer 1),



must be forced in the endo position of the second monomer unit. This crowding is illustrated in Fig. 3.

The steric compression required to force this group into the endo position must be very high; therefore, the incorporation of the third and subsequent monomer units is greatly inhibited or totally prevented. To illustrate the steric factors involved, this situation is entirely analogous to, and certainly at least as severe in steric repulsion as, 2,2-dineopentylnorbornane.



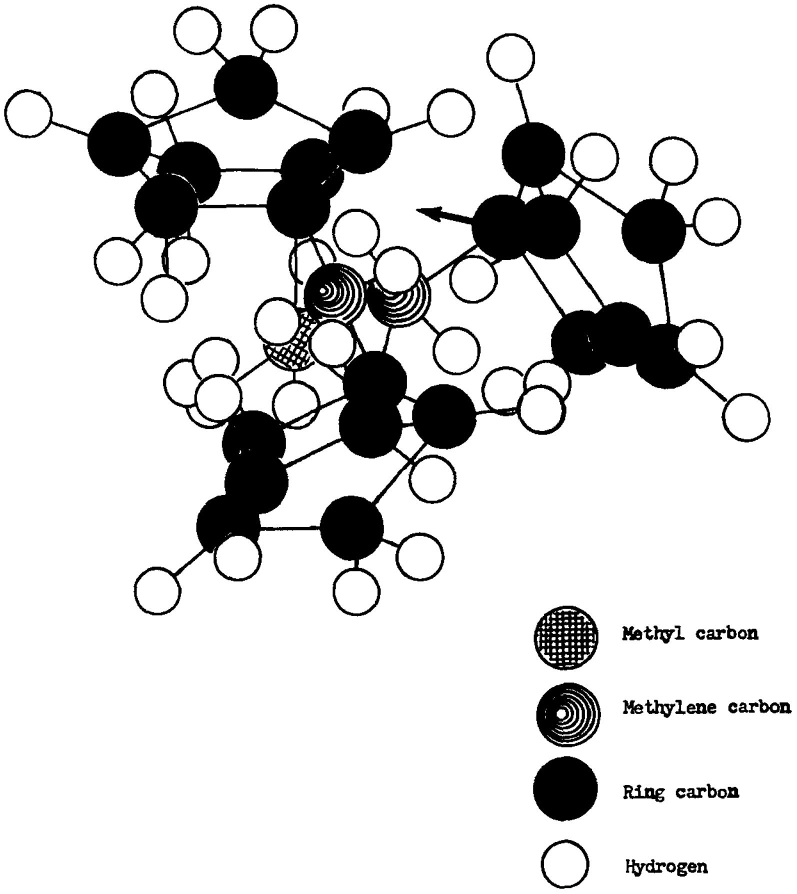
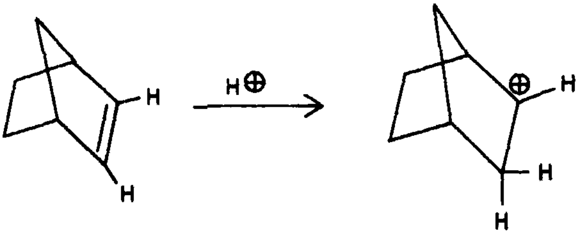


FIG. 3. Steric compression during propagation of methylenenorbornane.

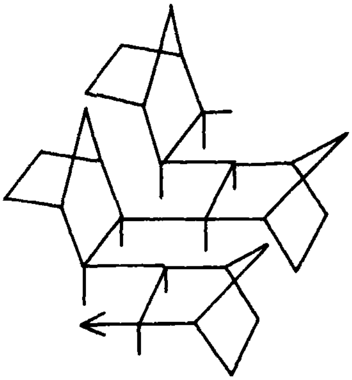
Certainly one must doubt that this particular molecule could even be prepared.

In summary, 2-methylenenorbornane does not polymerize to high molecular weight because propagation is greatly impeded by the compression of very large groups required for monomer addition.

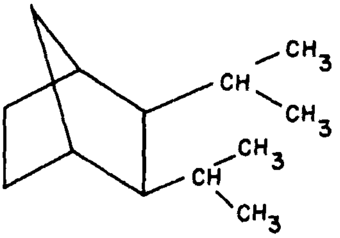
The driving force for norbornene polymerization has been discussed above. Certainly since norbornene polymerizes to relatively high molecular weight, it can be concluded that the steric factors during propagation are much smaller than with 2-methylenenorbornane. When norbornene is protonated, the resultant carbonium ion is devoid of major steric interactions; a hydrogen ion addition results in the incorporation of one endo hydrogen:



Similarly, when the protonated norbornene attacks a second norbornene monomer (again assuming an exo-exo attack combination), a carbon-carbon bond is established which is exo to both norbornane rings, and another hydrogen is incorporated in the endo position of the first monomer. All subsequent additions result in the same type of placements, so that the following structure is obtained:



The nature of the steric interactions resident in the norbornene system is illustrated by those present in 2,3-diisopropylnorbornane:



where both isopropyl groups are in the exo position. Clearly the steric interactions here, although large, can be accommodated far more easily than those encountered with 2-methylenenorbornane.

With norbornene, if the steric interactions were very high when endo attack occurred (with either carbonium ion or reacting monomer), it would be predicted that all established carbon-carbon bonds would be exo to the norbornane rings, and, therefore, the resultant polymer would be highly regular and crystalline. The fact that polynorbornene prepared with cationic catalysts is not crystalline suggests that steric inhibition of endo attack is not very great.

The steric compressions encountered in 2-methylenenorbornane are also encountered in the methylenecyclohexane and the β-pinene systems. Direct propagation is inhibited so that either only oligomerization occurs or higher-molecular-weight species are obtained via rearrangements.

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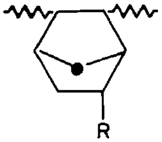
Zusammenfassung

Die kationische Polymerisation verschiedener olefinischer Bicyclo-(2,2,1)-heptanderivate wurde untersucht und die Struktur des resultierenden Polymeren bestimmt. Norbornen polymerisiert leicht zu löslichen Polymeren bei −78°, während 2-Vinyl-5-norbornen bei tiefer Temperatur (~ −78°) vorwiegend lösliche und bei höherer Temperatur (~ −30°) vorwiegend vernetzte Polymere liefert. Die wesentlichen Polymerisationsmechanismen für Norbornen und 2-Vinyl-5-norbornen sind einander ähnlich. In jedem Falle geht die Reaktion durch Öffnen der "endo"-Doppelbindung vor sich und die sich wiederholenden Einheiten sind



wobei R = H oder Vinyl ist. Der Unterschield in der Reaktivität zwischen der endocyclischen und exocyclischen Doppelbindung in 2-Vinyl-5-norbornen ist höchstwahrscheinlich auf Spannungen in der endocyclischen Doppelbindung zurückzuführen. Wenn die Reaktivität der exocyclischen Doppelbindung durch Einführung einer Methylgruppe erhöht wird (2-Isopropenyl-5-norbornen) beteiligen sich beide Doppelbindungen gleichzeitig an der Polymerisation und vernetzte Produkte werden erhalten.

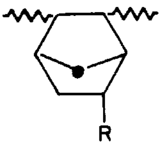
Konkurrenzexperimente zeigen, dass 2-Methylen-norbornane gegenüber Carboniumionen reaktionsfähiger ist als Norbornen.

Spektroskopische Untersuchungen (IR) bestätigen die schon von anderer Seite vorgeschlagene Struktur des Poly(2-methylen-5-norbornen).

Die Polymerisationsfähigkeit von olefinischen Bicyclo-(2,2,1)-heptanderivaten unter kationischen Bedingungen wird mit der von Cycloolefinen verglichen.

Résumé

On a examiné la polymérisation cationique des differents derivés oléfiniques du bicyclo-(2,2,1)-heptane et determiné la structure des polymères obtenus. Le norbornène polymerise facilement en polymère soluble à −78°C, tandisque le vinyl-2-norbornène-5 donne principalement un polymère soluble à basse température (~ −78°C) et un produit largement reticulé à des températures plus elevées (~ −30°). Les principaux mecanismes de polymérisation du norbornène et du vinyl-2-norbornène-5 sont analogues. Dans chaque cas la réaction procède par l'ouverture de la double liaison endo, et les unités répétitives sont



òu R = H ou vinyl. La différence de réactivitiés entre les doubles liaison endo et exo du vinyl-2-norbornène-5 est probablement dûe à la double liaison fatiguée endo. Quand la réactivité de la liaison exo est augmentée par l'introduction d'un groups méthyl (isopropenyl-2-norbornene-5), les deux doubles liaisons prennent part simultanément dans la polymérisation et on obtient des produits reticulés.

Des expériences analogues ont montré que le methylène-2-norbornane est plus réactif envers les ions carbonium que le norbornène.

Des études spectroscopiques (IR) confirment la structure du poly(methylène-2-norbornène-5) proposée par d'autres chercheurs.

On a comparé les polymérisabilités des derivés oléfiniques du bicyclo-(2,2,1)-heptane et des cycloolefins dans des conditions cationiques.

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